THE PHENOMENON OF DIMERIZATION OF ALKALI METAL VAPORS AND CALCULATION OF THEIR THERMOPHYSICAL PROPERTIES TO A TEMPERATURE OF 1500°C

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THE PHENOMENON OF DIMERIZATION OF ALKALI METAL VAPORS AND CALCULATION OF THEIR THERMOPHYSICAL PROPERTIES TO A TEMPERATURE OF 1500°C

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ABSTRACT   28369

This article describes the method to be employed in   /51*

an experimental investigation of the phenomenon of

dimerization in alkali metal vapors. It presents the

results derived from calculating the thermodynamic func-

tions of sodium vapors up to a temperature of 1500°C. AuTHoR

The calculation of thermodynamic functions of alkali metal vapors is complicated by the phenomenon of dimerization, which takes place according to the reversible reaction $Na_1 \gtrless 0.5\ Na_2$ in sodium, for example. As a result of dimerization, the alkali metal vapors represent a mixture of monoatomic and diatomic gases whose concentration is a function of temperature and pressure. It is absolutely necessary to know the values of the volumetric concentrations X_1 and X_2 of both forms of vapors, in order to calculate the thermodynamic functions of alkali metal vapors.

The phenomenon of dimerization in alkali metal vapors has been studied experimentally. Experiments have made it possible to determine the energy liberated during the dimerization process (dimerization energy). Let us investigate the main experiments.

The Deflection Method in a Magnetic Field

In contrast to their molecules, atoms of alkali metals have a magnetic moment (Ref. 1). This was studied by Lewis, who employed the method of

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* Note: Numbers in the margin indicate pagination in the original foreign
         text.

Stern and Gerlach (Ref. 2) to perform a spatial separation between bundles of atoms and molecules.

An alkali metal was vaporized in an oven, through whose opening a molecular beam passed containing monoatomic and diatomic alkali metal molecules. When the beam passed through a magnetic field having a particular configuration, atoms having a magnetic moment were deflected to both sides of the original direction; the molecules were not deflected. In order to measure the molecular beam intensity, after it passed through the magnetic field the beam was directed into a collector in the form of a cylindrical condenser.
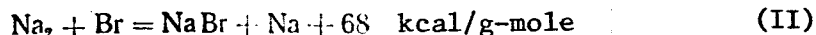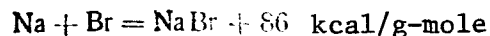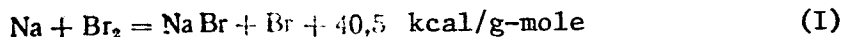
A long slit was cut into the flat side of the cylinder serving as the anode; the bundle of atoms and molecules entered the collector through this slit, and fell on the cathode. A tungsten filament located along the cylinder axis, which was heated by an electric current, served as the cathode.

As Langmuir (Ref. 3) has shown, when particles of alkali metal vapors strike an incandescent tungsten filament, they are ionized, and take on a positive charge. An electric current whose strength is proportional to the number of particles striking the cathode passes between the filament and the anode. The distribution of the bundle intensity I in the plane perpendicular /52 to the particle bundle can be measured by moving the collector in this plane. The results of these experiments performed at different temperatures have made it possible to determine the equilibrium constant of the dimerization reaction and the dimerization energy.

Luminosity Method

In these experiments (Ref. 4, 5), the luminosity of a rarefied mixture of gases reacting chemically was observed: vapors of an alkali metal and of any halide. Primary (I) and secondary (II) reactions thus took place; they can be

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written as follows for sodium and bromine:

$$Na + Br_2 = NaBr + Br + 40.5 \ \text{kcal/g-mole} \qquad (I)$$

$$Na + Br = NaBr + 86 \ \text{kcal/g-mole}$$

$$Na_2 + Br = NaBr + Na + 68 \ \text{kcal/g-mole} \qquad (II)$$

An investigation of the distribution of the reaction product precipitates and the luminosity intensity along a glass tube containing the gas has shown that the luminosity is caused by the secondary reaction $Na_2 + Br = NaBr + Na$. The luminosity intensity is proportional to the number of diatomic Na_2 molecules. The dimerization energy was computed from the intensity ratios at different temperatures.

Method for Observing Magnetic Rotary Spectra

When light which is polarized in a plane passes through a gas located in a magnetic field, rotation of the polarization plane occurs. This is particu- larly significant close to the absorption line, i.e., for light particles

TABLE 1

THERMODYNAMIC FUNCTIONS OF SODIUM VAPORS ON THE SATURATION LINE

t, °C	p_s, atm	c_{p_c}, $\dfrac{\text{kcal}}{\text{g·deg}}$	s', $\dfrac{\text{kcal}}{\text{g·deg}}$	r_1, $\dfrac{\text{kcal}}{\text{kg}}$	r, $\dfrac{\text{kcal}}{\text{kg}}$	s''_1, $\dfrac{\text{kcal}}{\text{g·deg}}$	s'', $\dfrac{\text{kcal}}{\text{g·deg}}$
400	$4.839 \cdot 10^{-4}$	0.306	0.0000	1060.0	1026.2	1.5747	1.5244
450	$1.725 \cdot 10^{-3}$	0.303	0.0218	1055.7	1012.1	1.4815	1.4213
500	$5.208 \cdot 10^{-3}$	0.302	0.0420	1051.3	997.7	1.4017	1.3325
550	$1.373 \cdot 10^{-2}$	0.301	0.0609	1047.1	983.4	1.3329	1.2555
600	$3.234 \cdot 10^{-2}$	0.300	0.7860	1042.9	969.1	1.2729	1.1885
650	$6.935 \cdot 10^{-2}$	0.300	0.0953	1038.7	955.3	1.2204	1.1301
700	$1.373 \cdot 10^{-1}$	0.300	0.1111	1034.5	941.3	1.1741	1.0790
750	$2.540 \cdot 10^{-1}$	0.301	0.1262	1030.3	929.0	1.1331	1.0341
800	$4.431 \cdot 10^{-1}$	0.303	0.1406	1025.9	916.5	1.0966	0.9947
850	$7.346 \cdot 10^{-1}$	0.305	0.1545	1021.5	904.6	1.0640	0.9598
900	1.165	0.308	0.1678	1017.0	893.1	1.0347	0.9291
950	1.776	0.311	0.1807	1012.3	882.0	1.0083	0.9018
1000	2.615	0.315	0.1933	1007.5	871.2	0.9846	0.8776
1050	3.735	0.320	0.2055	1002.4	860.7	0.9631	0.8560
1100	5.188	0.324	0.2174	997.1	850.6	0.9436	0.8369
1150	7.03	—	0.2289	991.6	841.1	0.9256	0.8199
1200	9.31	—	0.2401	985.9	830.7	0.9083	0.8039
1250	12.1	—	0.2509	980.0	821.1	0.8943	0.7900
1300	15.4	—	0.2614	973.9	811.2	0.8805	0.7774
1350	19.3	—	0.2716	967.6	801.4	0.8677	0.7652
1400	23.9	—	0.2815	961.1	791.3	0.8559	0.7544
1450	29.1	—	0.2911	954.4	781.3	0.8449	0.7444
1500	35.0	—	0.3005	987.5	771.1	0.8348	0.7360

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TABLE 1 (Cont.)

THERMODYNAMIC FUNCTIONS OF SODIUM VAPORS ON THE SATURATION LINE

i', $\frac{kcal}{kg}$	i'', $\frac{kcal}{kg}$	i_1, $\frac{kcal}{kg}$	i_2, $\frac{kcal}{kg}$	i_λ, $\frac{kcal}{kg}$	X_2	$d \cdot 10^2$, $\frac{kg}{m^3}$	c_p, $\frac{kcal}{g \cdot deg}$
145.0	1171.2	1205.1	792.1	412.96	0.043	0.021	0.844
160.3	1172.3	1215.9	802.1	413.77	0.056	0.071	0.883
175.0	1173.1	1226.6	812.2	414.55	0.069	0.202	0.912
190.4	1173.8	1237.6	822.2	415.31	0.083	0.507	0.918
205.4	1174.6	1248.3	832.3	416.04	0.097	1.126	0.908
220.4	1175.7	1259.0	842.4	416.76	0.111	2.340	0.889
235.4	1177.3	1269.9	852.5	417.46	0.125	4.451	0.865
250.5	1179.4	1280.7	862.6	418.13	0.138	7.922	0.836
265.6	1182.1	1291.5	872.6	418.77	0.150	13.320	0.805
280.8	1185.3	1302.3	882.9	419.40	0.162	21.317	0.773
296.1	1189.2	1313.1	893.1	420.01	0.173	32.673	0.739
311.6	1193.6	1323.9	903.3	420.59	0.183	48.191	0.708
327.2	1198.5	1334.8	913.6	421.16	0.193	63.723	0.679
343.1	1203.8	1345.5	923.8	421.70	0.202	95.155	0.651
359.2	1209.8	1356.3	934.1	422.22	0.210	128.22	0.625
375.5	1216.6	1367.1	944.4	422.71	0.217	168.59	0.602
392.0	1222.7	1377.9	954.7	423.18	0.224	217.10	0.579
408.7	1229.8	1388.7	965.1	423.64	0.230	274.00	0.557
425.6	1236.8	1399.5	975.4	424.10	0.236	339.80	0.537
442.7	1244.1	1410.3	985.8	424.54	0.241	414.72	0.518
460.0	1251.3	1421.1	996.1	424.97	0.246	499.87	0.501
477.5	1258.8	1431.9	1006.5	425.38	0.250	592.55	0.487
495.2	1266.3	1442.7	1016.9	425.78	0.253	694.35	0.475

close to the eigen frequency of the atoms. This phenomenon is called magnetic rotation of the polarization plane, and may be utilized to determine the dimerization energy (Ref. 6). The light from an electric arc was directed along a crossed analyzer and polarizer, between which a tube with vapors of the metal being studied was placed within the core of an electromagnet. Before the magnetic field was turned on, light did not pass through the crossed polarizer and analyzer, but – due to rotation of the light polarization plane – when the magnetic field was turned on the field of view became illuminated. It was thus possible to observe the magnetic rotary spectrum by means of the dispersion apparatus. This spectrum consists of separate lines caused by radiation of sodium atoms and a band caused by the radiation of diatomic sodium molecules. However, the individual bands overlapped to a lesser extent than in spectra obtained by other methods, and it was particularly easy to

study the spectral lines corresponding to the higher vibrational levels of molecule energy, thus facilitating an explanation of the dimerization energy.

Sittig (Ref. 7) has presented the most detailed summary of the physical thermal properties of sodium. He computed certain thermodynamic functions of sodium up to 1125°C. The basis of the computation was the dimerization energy of sodium at absolute zero temperature i_{d_o} = 9100 + 600 cal/g-atom, which comprises 0.79 eV per one Na_2 molecule. Table 1 presents the thermodynamic functions on the saturation line.

We supplemented the data in the table by the specific heat c_p, the vapor density d, and the specific entropy s', s_1'', s_2'' and s", respectively, of the condensed phase, the monoatomic and diatomic forms of saturated vapors, and /54 of an equilibrium mixture of both forms in saturated vapors:

$$s' = \int \frac{c_{p_c}}{T} dT + \text{const,} \quad \text{assuming} \quad s'_{400^\circ} = 0,$$
$$s_1^{\cdot} = s' + r_1/T, \quad s_2^{\cdot} = s' + r_2/T, \quad s'' = s' + r/T. \tag{1}$$

In order to construct i—s-diagrams up to 1500°, the quantities s', s_1'', s_2'', i', r_1, r_2, r, i_d, i_1'', i_2'', i" were extrapolated further along the saturation line, based on the tabular differences. All of the quantities were interconnected in accordance with relationships (1) and formulas

$$i_1^{\cdot} = i' + r_1, \quad i_2^{\cdot} = i' + r_2, \quad i_0^{\cdot} = i_1^{\cdot} - i_d, \quad i'' = i' + r$$

in the case of $\Delta i_1''$ = 4.965 Δt

By employing the values r_1 and r_2, the partial pressures p_1 and p_2 of the monoatomic and diatomic components, the total pressure $p = p_1 + p_2$, the volumetric concentrations $X_1 = p_1/p$ and $X_2 = p_2/p$ on the saturation line, and the equilibrium constant $K_p = p_1^2/p_2$ were computed by numerical integration of the Clapeyron–Clausius equation. This method verified the fact that the equilibrium constant values satisfy the equation

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$$K_p = K_{p_0} \, e^{\int_{T_0}^{T} \frac{46\,i}{RT^2}\mathbf{d}\, dT} \quad .$$

Computation of Entropy, Enthalpy, Specific Heat, and Density of Sodium Vapors

As a result of dimerization, the molecular weight μ of sodium vapors increases, $\mu = A(1 + X_2)$. In m grams of vapor there is $\frac{m}{A(1 + X_2)}$ moles, of which there are $X_1 \frac{m}{A(1 + X_2)}$ moles of monoatomic vapor and $X_2 \frac{m}{A(1 + X_2)}$ moles of diatomic vapor. Changing to gravimetric concentrations, we find that in 1 g of vapor there is $\frac{X_1}{1 + X_2}$ g of monoatomic vapor and $\frac{2X_2}{1 + X_2}$ g of diatomic vapor.

The specific enthalpy and entropy of sodium vapors additionally comprise the corresponding properties of their monoatomic and diatomic components:

$$i = \frac{X_1 i_1 + 2 X_2 i_2}{1 + X_2}; \quad s = \frac{X_1 s_1 + 2 X_2 s_2}{1 + X_2} . \qquad (2)$$

The volumetric concentrations X_1 and X_2 of the overheated vapor components are computed along the isotherms by means of the equations:

$$K_p = \frac{X_1^2}{1 - X_1} p \quad \text{and} \quad X_2 = 1 - X_1 .$$

The values of X_2 are shown graphically in Figure 1.

The enthalpy of an ideal gas depends only on temperature. Therefore, in formula (2), the enthalpy values i_1 and i_2 are soon to equal their values on the saturation line at the same temperature. The entropy s_1 and s_2 of both <u>/55</u> forms of vapors is computed along the isotherms according to the formulas:

$$s_1 = s_1^{\cdot} - \frac{R}{A} \ln \frac{pX_1}{p_s X_{1s}} , \quad s_2 = s_2^{\cdot} - \frac{R}{2A} \ln \frac{pX_2}{p_s X_{2s}} ,$$

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where p_s, s_1'', s_2'', X_{1s} and X_{2s} are the values of the corresponding quantities on the saturation line at the same temperature. The computed entropy values s_1 and s_2 satisfy the equation $s_1 — s_2 = i_d/T$ very well, which substantiates the reliability of the extrapolation we performed up to 1500°C. The i — s diagram for sodium is shown in Figure 2.

The specific heat c_p of sodium vapors can be determined by the numerical differentiation of enthalpy $c_p = \left(\dfrac{\partial i}{\partial T}\right)_p$. However, it is possible to avoid numerical differentiation and the difficulties it entails. By means of formula (2), we obtain

$$c_p = c_{p_f} — \frac{2 i_d}{(1 + X_2)^2}\left(\frac{\partial X_2}{\partial T}\right)_p. \tag{3}$$

By means of equations

we obtain

$$\frac{d \ln K_p}{dT} = \frac{46 i_d}{RT^2}, \qquad K_p = \frac{X_1^2}{1 - X_1}\, p$$

$$c_p = c_{p_f} + \frac{92}{R}\,\frac{X_1 X_2}{(1 + X_2)^3}\left(\frac{i_d}{T}\right)^2. \tag{4}$$

As Figure 1 shows, when sodium vapors are heated isobarically, the amount of diatomic molecules in them decreases. This is related to the absorption of energy, and therefore the effective specific heat c_p of sodium vapors is greater than their frozen specific heat c_{p_f}. This follows from formula (4).

The results derived from computing the specific heat of sodium vapors according to (4) are presented in Figure 3.

In the region under consideration, the frozen specific heat c_{p_f} of sodium vapors changes from 0.212 to 0.216 kcal/kg-degree, and the effective specific heat amounts to 0.918 kcal/kg-degree. It follows from this that dimerization in sodium vapors (and of other alkali metals) leads to a significant increase in their specific heat.
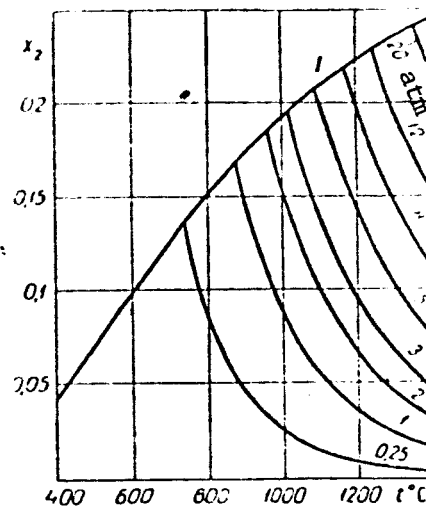
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Figure 1

Portion of X_2 Diatomic Molecules as a Function
of Temperature and Pressure. I – Saturation Line

The density d of sodium vapors is computed according to the equation of
state of an ideal gas $d = p\mu/RT$, $\mu = 23(1 + X_2)$. The computational results
are presented in Table 1.

<div align="center">Notation</div>

r_1 and r_2 – heat of evaporation pertaining to one gram-atom of the con-

densed phase, i.e., to 23 grams;

$A = 23$ – atomic weight of sodium;

$$c_{p_f} = \frac{X_1 C_{p_1} + 2 X_2 C_{p_2}}{1 + X_2}$$ – the so-called frozen specific heat of a mixture of

monoatomic and diatomic forms of sodium vapors, representing

the additive sum of their specific heats;

$$c_{p_1} = \left(\frac{\partial i_1}{\partial T}\right)_p = 0,216 \; \frac{\text{kcal}}{\text{kg} \cdot \text{degree}}$$ – specific heat of the monoatomic form of

sodium vapors;

c_{p_2} $\left(\frac{\partial i_2}{\partial T}\right)_p$ – specific heat of the diatomic form of sodium vapors; the
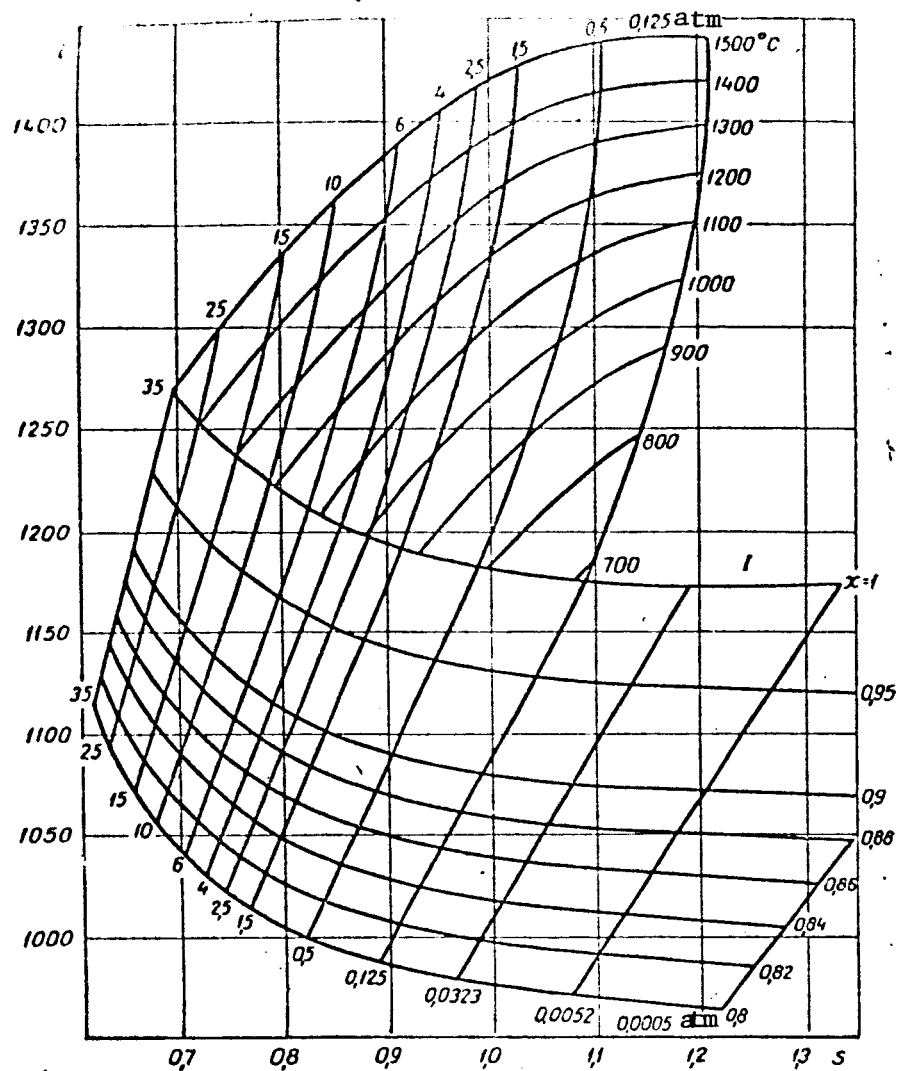
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Figure 2

i — s Diagram of Sodium (i, kcal/kg; s, kcal/kg·degree)
computed with allowance for vapor dimerization.
I - Saturation Line.

quantity changes very slightly with temperature (from

$$0.200 \ \frac{kcal}{kg \cdot degree} \ \text{in the case of } t = 400 \text{ up to } 0.208 \ \frac{kcal}{kg \cdot degree}$$

in the case of t = 1500°C);

$i_d = i_1 — i_2$ - dimerization energy;

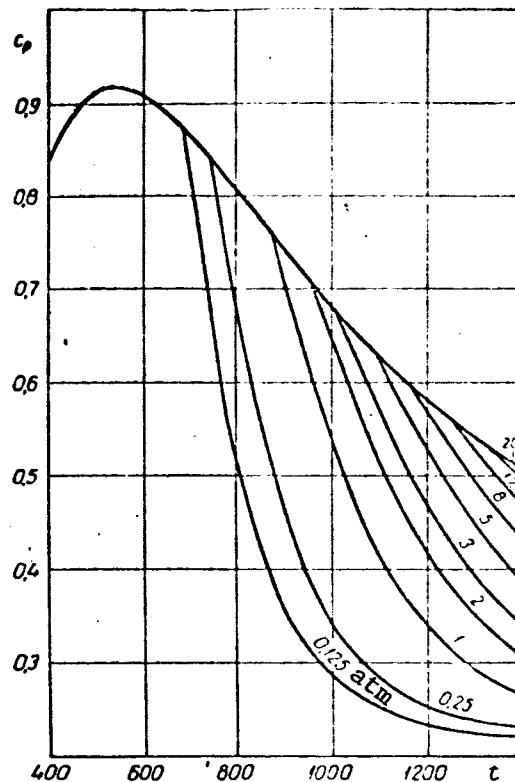c_{p_c} — specific heat of the condensed phase.

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Figure 3

Specific Heat in kcal/kg·degree of Sodium Vapors
as a Function of Temperature (°C) and Pressure (atm).

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